

**REMARKS**

**I. Interview Summary**

Applicant thanks Examiner Vasisth for the time and courtesy extended in conducting a telephonic interview with Applicant's representative on March 1, 2011. During the interview, the rejection under 35 U.S.C. § 103(a) over U.S. Patent No. 6,736,991 to Cohen et al. ("Cohen") in view of U.S. Patent 6,231,782 to Shimomura et al. ("Shimomura") were discussed. Specifically, Applicant's representative explained that Cohen and Shimomura fail to disclose or suggest the combination of the specific mineral oil, phosphorothionate, and phosphoric acid ester as claimed, and also discussed the unexpected beneficial results presented in Table 2 of the specification and the Rule 132 Declaration of Mr. Shimomura submitted with the Reply to Office Action filed November 16, 2009. No formal agreement was reached. The foregoing amendment and the following remarks reflect the substance of the interview.

**II. STATUS OF THE CLAIMS**

Applicant has cancelled claims 1 and 4-12, and has added new claim 13. The new claim is supported by the as-filed specification, e.g., paragraphs [0021], [0046], [0049], and Examples 1-6. No new matter has been introduced.

Claim 13 is pending and under examination.

As an initial matter, cancellation of claims 1 and 4-12 renders the rejection of these claims moot.

**III. New claim 13**

Applicant respectfully submits that new claim 13 is allowable over Cohen and Shimomura, considered alone or in combination, for at least the following reasons.

A reasonable expectation of success is required to support a conclusion of obviousness. M. P.E.P. § 2143.02. In order to have a reasonable expectation of success, at least some degree of predictability is required. M.P.E.P. § 2143.02(II). Applicant respectfully submits that the refrigerating machine oil as recited in claim 13 shows the unexpected beneficial results that were not predicted in the cited references, as discussed during the interview.

The present application discloses Examples 4-6, which correspond to the refrigerating machine oil recited in claim 13. See as-filed specification, paragraph [0129]. Specifically, the refrigerating machine oil compositions of Examples 4-6 each includes a combination of the mineral oil, phophorothionate, and phosphoric acid ester as recited in claim 13. As shown in Tables 2-3, Examples 4-6 (according to the claimed composition) showed marked improvement in wear resistance from the synergistic effect of the combination of the phophorothionate (A2) and the phosphoric acid ester (A1), as compared with Example 15, which included only the phosphoric acid ester (A1), and Example 16, which included only the phophorothionate (A2).

As discussed during the interview, these unexpected beneficial results would not have been achieved or predicted by Cohen or Shimomura. First, neither of the references discloses or suggests the combination of phosphorothionate and phosphoric acid ester as claimed. Cohen at column 7, line 3-5, discloses anti-wear compounds for refrigeration [being] alkyl-aryl or tri-aryl phosphates," but fails to disclose or suggest the specific combination of phosphorothionate and phosphoric acid ester. Shimomura at col. 9, lines 25-31 discloses several phosphorous compounds to be added to a refrigerating machine oil composition, but fails to disclose or suggest the combination of

phosphorothionate and phosphoric acid, as claimed. In the absence of this feature, neither Cohen nor Shimomura would lead one of ordinary skill in the art to arrive at the claimed invention and predicted the above-discussed beneficial results.

Regarding the claimed mineral oil, the Office Action asserted that Cohen at col. 3 lines 37-40 discloses naphthenic mineral oils and these mineral oils can be hydrotreated or refined to reduce sulfur and nitrogen-containing compounds such that "the sulfur and nitrogen compounds have been reduced such that the total sulfur and nitrogen is low at levels 0.05% or less and the %C<sub>A</sub> of the naphthenic mineral oil." Office Action at 3. During the interview, the Examiner continued to assert that Cohen's mineral oils encompass the mineral oil as claimed, and noted that concentrations of sulfur and nitrogen, and %C<sub>A</sub> can be adjusted independently, and thus a decrease in sulfur content would not affect %C<sub>A</sub>.

Applicant respectfully disagrees. Applicant has previously pointed out that the example oils disclosed in Cohen have a sulfur content of 200 ppm or 300 ppm and %C<sub>A</sub> of 14 or 12 (Cohen, col. 3, Table 1); and if these oils are filtered to reduce sulfur and nitrogen contents and the respective concentrations of both sulfur and nitrogen have been reduced to level of 50 ppm or lower, %C<sub>A</sub> must also be reduced to be out of the claimed range of 8-15 (perhaps down to 0). See October 26, 2010 Reply to Office Action, page 8; May 13, 2010 Reply to Office Action, page 9.

This Applicant's position is corroborated by the attached learned Treatise, "LUBRICANT AND SPECIAL FLUIDS," Vaclav Stepina et al., Tribology series 23, pages 134-147 (1992). The document describes that hydrogenation is one of the known procedures for refining mineral oils (page 139), and changes the compositions of

the mineral oils, e.g., sulfur content (%S) and aromatic content (%C<sub>A</sub>, RA) are reduced by hydrogenation (page 141). As an example, Table 3.4 at page 142 of the document shows that the value of %S of original oil is reduced from 1.18(before) to 0.063 (after), and that the value of %C<sub>A</sub> of original oil is reduced from 20.3 (before) to 5.1 (after). The document therefore supports that the concentrations of sulfur and %C<sub>A</sub> could not be adjusted independently; a decrease in sulfur content would affect %C<sub>A</sub>.

For these reasons, if the example oils disclosed in Cohen having a sulfur content of 200 ppm or 300 ppm and %C<sub>A</sub> of 14 or 12 (Cohen, col. 3, Table 1) are filtered such that the sulfur contents are reduced to "no more than 48 ppm," as recited in claim 13, then %C<sub>A</sub> must be reduced to be out of the claimed range of 10-15 (perhaps down to 0). Accordingly, Cohen neither discloses nor suggests a mineral oil as recited in claim 13.

For at least the above reasons, claim 14 is allowable over Cohen in view of Shimomura.

#### **IV. CONCLUSION**

In view of the foregoing remarks, Applicant respectfully requests reconsideration of this application, withdrawal of the rejections, and timely allowance of the pending claims.

Should the Examiner have any comments or questions, please contact the Applicant's representative at (202)408-4457.

Please grant any extensions of time required to enter this response and charge any additional required fees to Deposit Account 06-0916.

Respectfully submitted,

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GARRETT & DUNNER, L.L.P.

Dated: April 7, 2011

By: Hojung Cho  
Hojung Cho  
Ltd. Rec. No. L0596

**Attachment:** "LUBRICANT AND SPECIAL FLUIDS," Vaclav Stepina et al., Tribology series 23, pages 134-147 (1992).

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# LUBRICANTS AND SPECIAL FLUIDS

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6.1.64	Greases for Lubrication of Automobile Assemblies	695
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6.1.67	Greases for Lubrication of Automobile Assemblies	695
6.1.68	Greases for Lubrication of Automobile Assemblies	695
6.1.69	Greases for Lubrication of Automobile Assemblies	695
6.1.70	Greases for Lubrication of Automobile Assemblies	695
6.1.71	Greases for Lubrication of Automobile Assemblies	695
6.1.72	Greases for Lubrication of Automobile Assemblies	695
6.1.73	Greases for Lubrication of Automobile Assemblies	695
6.1.74	Greases for Lubrication of Automobile Assemblies	695
6.1.75	Greases for Lubrication of Automobile Assemblies	695
6.1.76	Greases for Lubrication of Automobile Assemblies	695
6.1.77	Greases for Lubrication of Automobile Assemblies	695
6.1.78	Greases for Lubrication of Automobile Assemblies	695
6.1.79	Greases for Lubrication of Automobile Assemblies	695
6.1.80	Greases for Lubrication of Automobile Assemblies	695
6.1.81	Greases for Lubrication of Automobile Assemblies	695
6.1.82	Greases for Lubrication of Automobile Assemblies	695
6.1.83	Greases for Lubrication of Automobile Assemblies	695
6.1.84	Greases for Lubrication of Automobile Assemblies	695
6.1.85	Greases for Lubrication of Automobile Assemblies	695
6.1.86	Greases for Lubrication of Automobile Assemblies	695
6.1.87	Greases for Lubrication of Automobile Assemblies	695
6.1.88	Greases for Lubrication of Automobile Assemblies	695
6.1.89	Greases for Lubrication of Automobile Assemblies	695
6.1.90	Greases for Lubrication of Automobile Assemblies	695
6.1.91	Greases for Lubrication of Automobile Assemblies	695
6.1.92	Greases for Lubrication of Automobile Assemblies	695
6.1.93	Greases for Lubrication of Automobile Assemblies	695
6.1.94	Greases for Lubrication of Automobile Assemblies	695
6.1.95	Greases for Lubrication of Automobile Assemblies	695
6.1.96	Greases for Lubrication of Automobile Assemblies	695
6.1.97	Greases for Lubrication of Automobile Assemblies	695
6.1.98	Greases for Lubrication of Automobile Assemblies	695
6.1.99	Greases for Lubrication of Automobile Assemblies	695
6.1.100	Greases for Lubrication of Automobile Assemblies	695

and higher polarity resins remain undissolved as a heavy phase. Selectivity can be controlled by adjusting the propane: asphalt ratio (as high as 10:1) and the temperature (up to 80 °C). *n*-Butane, which is less selective, can also be used. After the propane has evaporated from each of the two phases, the heaviest oils (propane deasphaltates or brightstocks) and propane asphalt are isolated. The process amounts to a selective extraction by a non-polar solvent.

Industrial exploitation has started of extractive distillation of residues by gases in a critical state. It makes use of the earlier observation that some fluids possess, in their super-critical states, the transport and diffusing properties of gases together with the solvent properties of liquids. This is true of non-polar fluids, e.g., methane to butane, as well as polar ones, such as nitrobenzene, carbon dioxide and ammonia (252, 255, 259).

Carbon dioxide dissolves, at 7.3 MPa and 31 °C the non-asphaltic parts of distillation residues and liberates them again when the pressure is lowered and the temperature is raised. This procedure (sometimes termed *decarbon*) is also suitable for extracting the non-asphaltic components from tars and from coal hydrogenation residues, for separating oil from used oils or from heavy crude oil deposits or asphalt sands (199).

### 3.2.1.2.2 Refining Processes

Refining substantially changes the chemical composition of lubricating oil distillates and can thus control the properties of raffinate (10, 259). Its primary effect is to reduce the concentration of the most polar constituents - oxygen, nitrogen and sulphur compounds, poly-nuclear aromatics and - to the extent that they are present - olefinic hydrocarbons, the products of local overheating. The object of refining processes is to improve colour, VI, long-term stability against ageing in storage and at operating temperatures, the reduction of cooking, etc. Unless refining is accompanied by profound chemical transformations (e.g., as in hydrogenation), distillation ranges and flash-point do not change significantly. Pour-point may rise somewhat if the paraffin wax crystallisation inhibitors (some resins) are removed, or if transformation into *n*-alkanes or long-chain alkyl substances occurs. However, it may decrease in the event of isomerisation or cleavage of *n*-alkanes or *n*-alkyls takes place. In contrast to distillation, both density and viscosity decrease. Amenable to treatment with additives improves.

Colour can be an indication of the depth of refining, but - as the people of experience say - colour does not indicate GOBT 2667-52 specifies a colorimetric method for oil colour determination. ASTM D-1500-64, IP 15686 and DIN 51 578 specify visual methods. The colour of the oil in a test-tube of prescribed dimensions is compared with a scale of coloured glass strips. The standards are numbered and the test result is defined as the ASTM colour and the number of the matching glass strip. Accuracy is 0.5 unit up to 8. Oils of colour exceeding 8 are diluted with kerosene in a specified ratio. The IP 17 method, which employs a Lovibond Comparator (officially used principally for measuring the colour of beer), is less frequently used; the colour of the oil is compared with the colour formed by combination of red, yellow and blue standard glass strips with numerical gradations, e.g., 2 red, 3 yellow, 1 blue, of red, yellow and blue standard glass strips with numerical gradations, e.g., 2 red, 3 yellow, 1 blue,

etc. The ASTM D-156 method is also suitable for determining the colour of "white" oils: the oil sample is compared with coloured glass standards numbered +30 to -15. The higher the colour, the higher the number.

Another criterion is the amount of residue produced on "carbonisation". This type of test consists in determining the percentage of solid formed by the thermal decomposition of the oil in the absence of air under specified conditions. Two methods are used to produce the Carbonium Carbon Test (CCT), used more in Europe, and the Ramondom Test, used in the USA. The CCT method is described in ASTM D-189 and the ideal test CSN 65 6210, GOBT 5987-51 and DIN 51 551. The carbonisation residue is determined by the thermal decomposition of a 10 g oil sample in a porcelain crucible under prescribed heating conditions. The Ramondom Test is specified in ASTM D-524 and IP 14. The carbonisation residue is determined by heating, vaporising and decomposing the oil sample in a furnace at 550 °C. The CSN 65 6211 carbonisation test is identical to the CCT, except that a 2 g sample is used in a smaller porcelain crucible.

The assessment of other quality criteria (VI, oxidation stability, etc.) which relate to refining is described elsewhere in this book.

The main types of refining processes now employed are refining with chemical agents, selective solvents, adsorbents and hydrogen (hydrogenation).

### Refining with Chemical Agents (10c)

This is the earliest refining process. The main agents used are sulphuric acid and sometimes oleum or sulphur trioxide, or, more rarely, other agents such as anhydrous aluminium trichloride (10c). Refining with acid agents is followed by neutralisation, usually with calcium hydroxide or caustic alkali.

Sulphuric acid causes polymerisation, condensation and, at elevated temperatures and concentrations, sulfonation and oxidation. It also partly acts as a selective solvent. Saturated and mono-nuclear aromatic hydrocarbons are comparatively little attacked. The unsaturated components, e.g., thermally-changed lubricating oils, produce acid esters and polymers, which pass into the acid layer. Poly-nuclear aromatics tend to undergo condensations and sulfonations; the products of these transformations also pass into the acid layer. The same applies to oil resins and nitrogenous compounds, oxygen and sulphur compounds. They partly dissolve in the acid, are partially converted into ionic species, condense or are sulfonated. The non-aromatic naphthenic acids dissolve in the acid, whilst the aromatic ones can, additionally, be sulfonated. Nitrogenous bases are neutralised and pass into the acid. However, the selectivity of these processes is rather poor.

The process produces two layers: a less polar raffinate and a layer of acid sludge (acid resins). The layers are separated by settling, centrifugation or electrostatic processes. The raffinate is extracted with caustic alkali and washed with water. After drying, it may be further post-refined with bleaching agents to make the final raffinate. This is a product showing good quality parameters, although the VI is not much higher than that of the distillate. The acid sludge is a troublesome waste. It is hard to handle, corrosive and undergoes further condensation and oxidation reactions connected with the formation of asphaltenes, carbens and carbidols, releasing irritating sulphur dioxide. Disposal procedures are still not satisfactory, which is one

of the reasons why no new plants are being erected. Existing plants, as long as they continue in operation, are used for the production of light beamers, turbine, transformer and similar lubricants from wax-free or de-waxed distillates.

### Reclaiming Used Oils

Refining with sulphuric acid is also used for the reclaiming used engine and some industrial oils (11). Reclaimed oils may achieve composition and attributes similar to the original oils, however, their refining is somewhat troublesome. Most of the problems stem from the products of physical and chemical ageing and by contaminants and additives present. One of the procedures worth mentioning is the Czochotlovak process which involves the transport of these contaminants into a water-glass solution, whereby the contaminants are adsorbed on the colloidal silicic acid produced by hydrolysis in the water layer (12). Waste oils may also be decarbonised and dewaxed with surfactants, e.g., oxyethylated phenol, and after settling, subjected to conventional treatment (13). However, even for the treatment of waste oils, sulphuric acid processing is being replaced by other processes, such as solvent treatment, hydrogenation or combinations of these (257).

Modern reclaiming techniques based on combined distillation, desasphalting, solvent refining and, chiefly, hydro-refining processes are capable of producing reclaimed oils which match the quality of virgin raffinates. The quality of a reclaimed oil used in engine lubricants is shown in Table 3.2.

Table 3.2. Quality Specification for a Re-refined Used Engine Oil

Parameter	ASTM Method	Limits
Flash-point	D-92	as in virgin raffinate
Insoluble Substances	D-893	0.01% by weight max.
Sulphated Ash	D-874	0.01% by weight max.
Glycols	D-2682	absent
Sulphur	D-2652	0.25% by weight max.
	D-129	50 p.p.m. max.
Phosphorus	-	100 p.p.m. max.
Chlorine	-	0.01% max.
Water	-	0.15 TAN max., strong
Neutralisation No.	D-664	base, 0, strong acids, 0.
Aniline Point	D-611	93 °C min.
Viscosity Index	D-2270	90 min.
Trace Metals	X-ray fluorescence, 200 p.p.m. max.	atomic absorption, or emission spectroscopy

### The Manufacture of White Oils

Medicinal oils must not contain aromatics. Purging sulphuric acid and, more recently, sulphur trioxide are used for their manufacture, as well as for the

manufacture of technical white oils. After pre-treatment with acid and removal of the acid sludge, or after a pre-treatment with hydrogen, the aromatics and resins are sulphonated by repeated dosages of oleum or SO<sub>3</sub>. The sulphonic acids formed pass partly to the oil and partly to the acid layers. The oil layer is extracted with an alcoholic solution of caustic alkali. The recovered "manogany" sulphonates are oil-soluble and are valuable raw materials for the manufacture of detergent additives for oils and emulsifiers. The "green" sulphonates extractable from the water layer are inferior, but cheap wetting agents. Again, in the manufacture of white oils, hydrogenation is displacing acid-refining if sulphonates are not required (22).

### Solvent Refining

The main criterion of solvent power is similarity of chemical composition or of molecular mass.

Solvent refining consists in the separation of wax-free oil cuts into two layers: one rich in less-polar components, poor in solvent, the raffinate layer, the other rich in polar components and solvent, the extract layer. After flashing off the solvent, the raffinate comprises the high-grade part of the original oil, characterised by high VI (up to 100, but rarely more), light colour and high stability against ageing, whilst the extract is that part with undesirable attributes (with few exceptions) - dark colour, sticky consistency, high density (even over 1,000 kg m<sup>-3</sup>), high viscosity, low or even negative VI, low resistance to ageing and a tendency to form carbonisation residues.

Solvents are selected according to their selectivity and solvent power. Selectivity is that property which distinguishes between wanted and unwanted components and provides the means to separate them; solvent power defines the quantity of solvent necessary to transfer the more soluble components into the extract. Both properties change with increasing temperature: selectivity decreases, solvent power increases (with a few exceptions, e.g., propane in the desasphalting process). At the critical temperature, one phase is formed and no separation occurs. Thus, by changing the temperature and the solvent to oil ratio, the desired depth of refining can be achieved.

The most common selective solvents are furfural (FF), suitable for all oil stocks (even gas oils and brightstocks), and phenol (Ph), more used for waxy oils than wax-free, and for more heavy than light cuts. More recently, N-methylpyrrolidone (NMP) has also been used. It has good selectivity (FF > NMP > Ph), solvent power (NMP > FF > Ph), stability (NMP > Ph > FF), biodegradability (NMP > Ph > FF) and lower toxicity. This all leads to lower investment and operating costs, so that many furfural and especially phenol plants are being converted to NMP (261). Other solvents are known (e.g., wet trisecol, SO<sub>2</sub>, benzene), but they have only found limited application or are now regarded as out-dated.

### Solvent Precipitation

In selective precipitation processes, non-polar solvents precipitate the most polar asphaltenes and oil resins in oil distillates and distillation residues, in oils so deasphalted wax components (as in some de-waxing processes), and polar oxidation products and additives from used oils. The less polar or light constituents are transported into the solvent. Conventional precipitants are alkanes, chiefly liquid propane. The lighter ethane precipitants too much of the oil with the asphalt, *n*-butane to hexanes, on the other hand, precipitate selectively only the asphaltenes and the most condensed resins of highest softening point. The effects of both polar and non-polar solvents may be combined in one unit operation. Thus, in the Duosol process for distillation residues, asphaltenes and resins are precipitated by propane and the propane simultaneously extracted with a phenol-cresol mixture.

### Adsorption Refining Processes

Adsorption refining is based on the adsorption of polar substances on the surface of a polar adsorbent, for example, natural or synthetic aluminosilicates, silica gel, alumina or bauxite. These processes nowadays are mainly used for reclaiming used oils after acid or solvent refining to remove refining agent and other impurities and colour. Although it is possible, in adsorptive refining, to separate the desirable from the undesirable oil components better than with solvent refining, and to obtain higher yields of raffinate, it is rarely employed as the main refining process (15).

Adsorptive refining with high surface area graphitic may become the exception. Here, the *n*-alkanes (oil waxes) and polynuclear aromatics are primarily adsorbed. Oils of substantially higher VI and, particularly, low viscosity at low temperatures are recovered (210).

Adsorptive refining is classified into contact and percolative processes. In contact processes, the oil is mixed with a minor proportion of the finely divided adsorbent (1 - 3%) at below 100 °C in the cold-contacting process, before separation of the spent adsorbent. This variant is used for cleaning light industrial oils (turbine oils, electroinsulating oils, etc.) as well as reclaiming these oils. The hot contacting process proceeds at temperatures up to 340 °C, up to the flash-point of the oil but never above its decomposition temperature, with the object of achieving more thorough reclaiming of engine oils, compressor oils and, generally, heavy oils and bitustocks.

Percolation processes consist in filtering the oil at lower temperatures through a stationary bed of relatively coarse-grained adsorbent and recovering the first eluates, which become gradually darker as the percolation proceeds. The later eluates are returned to the oil-stock feed-tank.

Adsorptive refining improves oil colour, brightness and oxidation stability, and removes water and contaminants which might be corrosive.

A high-quality oil should not contain water and physical contaminants. CSN 65 6231 and GOST 1541-74 specify a qualitative test for water present in oil. The sample is heated in an oil bath to 150 °C,

If water is present, the oil splinters and foams. Quantitative distillation methods are specified by CSN 65 6063, GOST 1594-69, ASTM D-95, IP 74 and DIN 51582. The oil is diluted with a solvent, e.g., a paraffinic spirit, plus oleic acid to suppress foaming, or xylene, and distilled. The solvent vapour plus entrained water vapour is condensed and accumulated in a gauge-glass. The volume of water is measured after phase separation. Determination of water by potentiometric titration with Karl Fischer reagent is specified in ASTM D-1244 and DIN 51-777.

Physical contaminants in oils are determined by CSN 65 6219, GOST 6370-59 and DIN 51592. Solid particles are filtered off from a solution of the oil in a suitable solvent, such as *tert*-xylene-ethanol mixture, or hexane.

Adsorption processes used to be common as the final treatment before oil-blending to required quality. Problems of disposal of spent adsorbent have contributed to their replacement by hydrogenation processes.

### Hydrogenation (16)

Unlike acid refining and solvent refining, hydrogenation produces various depths of conversion of undesirable components into lighter, low-viscosity and heavier, high viscosity hydrocarbons. No troublesome wastes are produced.

Three types of hydrogenation process may be distinguished: hydrofinishing, hydrofining and high-pressure hydrogenation or mild hydro-cracking. All three types proceed at higher temperatures, from 250 to 420 °C and at pressures from 2 to 20 MPa, both parameters higher and lower in exceptional cases due to the use of catalysts, which are usually transition metals and their compounds (oxides, sulphides) on a more or less acid substrate, in a hydrogen environment and with the consumption of hydrogen. In the hydrofinishing processes, the last traces of impurities remaining in the oil after acid or solvent refining are removed. In hydrofining, some deeper transformations occur, including partial saturation of aromatic nuclei and partial hydrogenation of O, S and N-containing components. In the HP-hydrogenation, at the upper temperature and pressure limits - virtually a mild hydrocracking process - deep transformations occur, almost complete hydrogenation and hydrogenolysis reactions, isomerisations and cracking reactions.

### Hydrofinishing and Hydrofining

Typical operating conditions for these processes are temperatures of 250 to 370 °C, pressures from 2 to 7 MPa, liquid-hourly space velocities (LHSV) 0.5 to 3 h<sup>-1</sup>, hydrogen-to-feed ratios 300 to 800 vol. H<sub>2</sub>/vol. feed, and hydrogen consumption 5 to 80 vol./vol. of feed, the lower values for hydrofinishing. Typical catalysts are cobalt molybdates or more active nickel and nickel-cobalt molybdates on a slightly acidic alumina (e.g., 10 to 15% MoO<sub>3</sub>, 3 to 5% CoO, 4 to 5% NiO) for hydrofinishing and less active catalysts, e.g., for hydrofinishing. Yields of raffinate are up to 98% in hydrofinishing and less in hydrofining. The light by-products are flashed off within the unit.

In hydrofinishing, no substantial chemical transformations take place. In hydrofining, substantial reduction of oxygen compounds and of 20 to 70% of sulphur compounds (in terms of sulphur content) occurs - hence the synonymous designation hydrodesulphurisation. Nitrogen compounds are nrobisecome, heavy compounds being converted into light compounds (17) which contribute to accelerated deactivation of acid centres in the catalyst. Resin concentration is reduced, as is carbonisation residue (up to 50%), colour is improved, viscosity slightly reduced and VI slightly increased. Stability to ageing and additive response are increased. In this respect, medium pressure hydrogeneration is a mild refining process which normally follows, but may precede, solvent refining of oil distillates.

#### High-Pressure Hydrogeneration - Hydrocracking of Oils

The importance of HP-hydrogeneration as the main treatment of lube oil distillates or desphalied distillation residues is increasing. It enables oils to be obtained with a high VI or even extremely high VI (XCHVI - e.g. up to 150 from hydro-cracked slack waxes). This process was probably first introduced under field conditions in Czechoslovakia in 1961: about 40% of lube oils are now products of HP-hydrogeneration. Typical operating conditions are temperatures 370 - 420 °C, pressures 10 - 30 MPa, LHSV 0.5 - 1.5 h<sup>-1</sup>, hydrogen-to-feed ratio 900 - 2,000 vol/vol. and consumption of hydrogen 80 - 250 vol/vol. Even at the same VI, the composition of hydrocracked oils differs significantly from that of solvent raffinate, as shown by Table 3.3 (21, 200). Catalysts used are more active than those in hydrofining, being mostly sulphides of transition metals, like MoS<sub>2</sub>, WS<sub>2</sub>, MoS<sub>2</sub>/NiS, and, in the case of pre-hydrogenated stocks in a second stage of hydrogeneration, including nickel and noble metals, Ni, Pd, Pt, all on γ- or γ-alumina or natural or synthetic aluminosilicates, both amorphous and crystalline, e.g. molecular sieves (3X/Al<sub>2</sub>SiO<sub>5</sub>OH) (22, 23). Pore dimensions and the acidity of the catalysts are carefully balanced so as to impede rapid deactivation and to guide the transformation in the desired direction. The metallic component enhances hydrogenation, leading to cycloalkanes and allylated and cycloallylated benzenes from O, S and N constituents, resins, polynuclear aromatics and to a certain extent polycyclicalkanes (26f). The noble metals enhance the hydrogenolytic opening of cycloalkane rings to branched-chain alkyis. The acidic component facilitates cleavage, producing hydrocarbons with lower viscosities and the isomerisation of cyclohexanes to cyclopentanes and to branched, saturated hydrocarbons with lower pour-points. It also enhances the hydrocracking of substances with electron-donor properties (containing O, S, N and double bonds) because of their stronger adsorption on to electron-acceptor centres. However, this increases the risk of catalyst deactivation by carbonaceous products (so that pore dimensions must be optimised (22)).

Hydrogeneration is thermodynamically a low temperature process, but its kinetics require higher temperatures. This contradiction must be compensated by higher pressures. Active catalysts permit temperatures and pressures to be decreased. Under

Table 3.3. Comparison of Duo-Sol Solvent Extraction and Hydrocracking of Romashkino-Mukharovo Crude (22)

	Duo-Sol Solvent		Hydrocracking
	Extraction		
Viscosity (mm <sup>2</sup> .s <sup>-1</sup> ) at 50 °C	31.31		35.13
VI	90		91
Pour-point (°C)	-12		-10
Chemical Composition by Mass-Spectrometry, % weight			
Alkanes	20.2		21.1
Monocyclicalkanes	5.6		12.7
Dicyclicalkanes	11.3		16.4
Higher Alkanes	28.5		31.6
Total Cycloalkanes	45.4		60.7
Alkybenzenes	8.2		5.5
Iodanes + Terallus	5.6		4.1
Dicyclobenzenes	3.6		3.2
Naphthalenes + Tricyclobenzenes	2.2		0.8
Acenaphthenes + Biphenyls	4.2		2.2
Fluorenes + Acenaphthalene *	2.9		2.0
Dicyclonaphthalenes	26.7		17.8
Total Aromatics			
Benzobiphenes	3.8		0.0
Dibenzobiphenes	2.7		0.0
Total thiophenes	6.5		0.0
Resins	1.2		0.4

otherwise identical conditions, an increase in temperature increases hydrogen consumption and affects the composition of the hydrograte (22). Reducing the pressure, under otherwise identical conditions, cause hydrogen consumption to decrease, prolongs the operating cycle, but adversely affects the hydrogenation of aromatic hydrocarbons and heteroatomic components, so that the residual concentration of heavy aromatics and resins in the product is higher. So to achieve products of the same VI with less active catalysts, the temperature must be raised.

Hydrogeneration changes the composition of all homogeneous oil groups (24) - see Table 3.4 and 3.5. The viscosities, densities, sulphur content (%S) and aromatic content (% C<sub>9</sub>, R<sub>9</sub>) are all reduced, whilst VI, hydrogen content, concentration of cycloalkane compounds and rings (% C<sub>9</sub>, R<sub>9</sub>) are increased. The true (paraffinic) pour-point of oils are increased, whilst the false (viscosity) pour-points are decreased. This suggests that it may be advantageous to subject to HP-hydrogeneration those stocks which are roughly unified as a group in terms of their constituents, and use processes which simplify the composition of the feed, e.g., hydrofining, or to proceed in more than one stage.

Table 3.4. Changes in the Composition and Properties of an Oil and Its Chromatographic Constituents - before and after Hydrocracking (24)

Oil	original		alkanocyclanes		monoaromatics		diaromatics		polyaromatics	
	before	after	before	after	before	after	before	after	before	after
Yield (% vol.)	100	100	32.8	71.9	26.8	16.2	17.7	6.45	9.7	0
Density at 20 °C (kg.m <sup>-3</sup> )	919	879	856	856	899	898	995	987	1049	-
Viscosity at 50 °C (mm <sup>2</sup> .s <sup>-1</sup> )	53.4	24.3	22.8	20.0	31.7	22.4	357.5	71.0	736	-
VI	58	91	107	121	68	68	-122.	50	-415	-
%H	12.4	13.0	14.1	14.0	12.63	12.93	10.8	11.2	9.81	-
%S	1.18	0.063	0.033	0.0015	0.67	0.063	2.89	0.472	3.13	-
Pour-point (°C)	-18	4.5	-9	6.2	-17	17.5	8	-13.5	12	-
Composition by Type (mol%) <sup>a</sup>										
%C <sub>A</sub>	20.3	5.1	0	0	15.0	155.1	40.9	33.3	44.8	-
%C <sub>M</sub>	20.7	36.4	29.4	30.7	22.6	25.2	18.1	29.4	34.5	-
%C <sub>T</sub>	59.0	58.5	70.6	69.3	62.4	59.7	41.0	37.3	30.7	-
R <sub>C</sub>	2.58	2.37	1.86	1.82	2.39	2.52	4.04	3.53	5.20	-
R <sub>A</sub>	1.08	0.21	0	0	0.80	0.77	2.68	1.68	2.58	-
R <sub>N</sub>	1.58	2.16	1.80	1.82	1.59	1.75	1.36	1.85	2.62	-

<sup>a</sup> Diaromatics and Polyaromatics according to Hazelwood.

Table 3.5. Changes in Viscosity, Viscosity Index and Chemical Composition at Increased Hydrogenation Severity (21)

	Hydrocracked Oils from Vacuum Distillate				Hydrocracked Oils from Propane Deasphaltate		
Viscosity Index	91.2	98	115	123.5	83.5	121	127
Viscosity (mm <sup>2</sup> .s <sup>-1</sup> ) at 50 °C	35.13	28.13	22.94	19.9	88.27	35.92	29.63
Chemical Composition by Mass-Spectrometry (% weight) <sup>a</sup>							
Alkanes	21.1	22.4	28.7	45.1	15.1	37.5	32.8
Monocycloalkanes	12.7	21.6	26.7	19.6	17.4	21.7	29.0
Dicycloalkanes	16.4	19.1	19.6	10.2	9.5	18.0	18.4
Higher cyclanes	31.6	16.0	12.3	6.0	23.1	7.6	5.3
Cyclanes	60.7	36.7	38.6	35.8	50.0	47.3	55.7
Alkylbenzenes	5.5	9.0	6.4	7.0	17.2	9.3	4.9
Indanes + tetralins	4.1	4.7	2.5	5.4	7.5	2.5	3.8
Dicyclanobenzenes	3.2	3.3	1.4	2.3	5.1	1.2	0.9
Naphthalenes + tricyclanobenzenes	0.8	1.0	0.4	0.8	1.7	0.4	0.4
Acenaphthenes + diphenyls	2.2	0.9	0.7	1.5	1.2	0.6	0.6
Fluorenes + acenaphthalenes + dicyclanaphthalenes	2.0	1.8	0.8	1.5	1.8	0.7	0.1
Aromatics	17.8	20.6	12.2	18.5	34.5	14.7	10.7
Resins	0.4	0.3	0.5	0.6	0.4	0.5	0.8

<sup>a</sup> Relative data.

HP-hydrogenation (i.e., mild hydrocracking) enables high-grade and high-VI oils to be produced economically. Oils of this quality cannot be obtained by solvent refining, and even if they could, yields would be very low. The superiority of HP-hydrogenation consists in the possibility of obtaining oils with VI's up to 130 (exceptionally even higher) from almost any type of oil in high yields, in better utilisation of by-products (high-quality motor fuels and light lube oil cuts), good response to additives, lower volatility at the same viscosity and lower biological activity. Less convenient characteristics are poorer stability to light, higher corrosivity after oxidation and lower solvent power for polar substances, e.g., for oxidation products and additives.

The overall concentration and type of aromatic compounds, together with the concentration of sulphur and nitrogen compounds, are decisive factors in the properties in service of HP-hydrogenates, particularly in respect of thermooxidative stability. This stability grows up to a certain critical concentration of aromatics, then when this is exceeded it becomes much worse (169, 202). The relative molecular mass of the aromatics, the number of nuclei present and the concentration of sulphur compounds are also very important. The heavier the aromatics and the greater the concentration of sulphur compounds, the lower is the critical concentration (170, 171). Hydrogenates containing less than 5% of aromatics have a rather poor oxidation stability. In comparison with selective raffinates, hydrogenates are especially sensitive above 210-220 °C. This manifests itself by a tendency towards more serious carbon deposition in the first piston grooves with engine oils formulated from hydrogenates. This inconvenience may be overcome by optimising the structure and content of additives (anti-oxidants, detergents and dispersants) or using doped blends of selected raffinates and HP-hydrogenates.

Oils made from HP-hydrogenates usually have inferior anti-wear properties. This is due to the absence of polar components. Suitable additives enable this disadvantage to be overcome (172).

A further drawback associated with HP-hydrogenates is low solvent power for additives, particularly for some polymers, and for the polar products of ageing. This also is due to the low concentration of aromatic components, which is also responsible for a high aniline point of HP-hydrogenates and for shrinkage of rubber seals and packings (aromatic content which is too high causes swelling).

Pale-coloured sludges are formed in hydrocracked oils by the action of light. The constituents which are responsible for this effect have not yet been identified, but compounds with a reactive tertiary carbon, traces of olefins originating from dehydrogenation, or some hydroaromatic or polyaromatic compound are suspected. Light stability can be improved by removing or converting these components, e.g., by low-temperature hydrogen after-treating in a fine-finishing converter, by catalytic conversion on molecular sieves in the absence or presence of added alkenes (220) (which also improves resistance to ageing), by further reducing the concentration of heavy aromatics, e.g., by clay treatment, and by using suitable anti-oxidants, because the natural anti-oxidants (some resins, some poly-nuclear aromatics) have to a large extent been removed.

The preferred feedstocks for HP-hydrogenation include heavy oil distillates, desasphalted vacuum distillation residues and, more recently, distillation residues from high-severity cracking to make motor fuels. Slack waxes may even be hydrocracked to XHVY oils. Specific processes have been developed (22). Some have been commissioned or are being promoted in the USA (Chevron - 261), France and Germany (the IFP process - 262), the Soviet Union (263), East Germany (264) and in Czechoslovakia (the NVOI process - 265). Yields up to 80% of viscous products may be attained. Relatively low viscosities limit their applications, although viscosities up to about 12 mm<sup>2</sup>s<sup>-1</sup> at 100 °C can be achieved by hydrogenating brightstocks. So a wide variety covering almost 98% of the lube oil range can be produced, with the exception of heavy compressor and cylinder oils - light distillates of lower VI and low pour-point for oils of ISO VG 2 to 15 grades, medium distillates or hydrogenates for bearing, turbine, hydraulic, transformer, white and similar oils and heavier hydrogenates emanating from hydrogenated brightstocks or hydrogenates of higher viscosities from oil distillates as components of engine oils improved with suitable additives or with predominantly di-nuclear aromatic oil components or simply with heavier solvent raffinates. These hydrogenates must be freed from light components, which affect the thermooxidation stability of the product. As by-products, saturated and virtually sulphur-free motor fuels and refined waxes with improved filterability are obtained. HP-hydrogenates are serious competitors of synthetic polyalphaolefin (PAO) oils, with the advantage of lower price.

#### De-Waxing Processes

Solvent dewaxing is the dominant process in the recovery of oils of low pour-point and good rheological properties at low temperatures from waxy distillates and raffinates. The oil is diluted with the solvent, chilled to low temperature and the separated wax crystals filtered off (167).

Suitable solvents include propane, particularly for residual oils such as propane desasphaltes, ethane, particularly for producing oils of very low pour-point, or so-called solvent/anti-solvent mixtures. The anti-solvent precipitates the wax and promotes the formation of wax crystals which are easily filtered and washed; the solvent dissolves the oil which is occluded in the filter cake. Examples of anti-solvent/solvent pairs are methylcetyl ketone (2-butanone)-toluene and 1,2-dichloroethane-dichloromethane. Precipitating and dissolving effects are continued in methylcetyl ketone (4-methylpentan-2-one).

Light oils may also be de-waxed by processes based on other principles (168): adsorption of *n*-alkanes by molecular sieves, formation of area adducts with alkanes and degradation of paraffins by fermentation. These processes are of limited importance.

Oils of extremely low pour-points and low viscosities at low temperatures (for bearing, hydraulic, transformer and other oils) are still mostly manufactured by refining wax-free cycloalkanic oil cuts. Oils with similar properties may also be

obtained by de-waxing waxy cuts at very low temperature. Since the latter method is expensive, and wax-free oils are scarce, processes based on combinations of conventional de-waxing and the further decrease of oil pour-points and viscosities at low temperatures by adding pour-point depressants have been developed. The advantage of such a procedure is that oils produced in this way have lower viscosities at low temperatures than oils made from cycloaliphatic crudes and that they retain relatively high VIs and the required pour-points.

These low pour-point oils, however, have limited applications. They cannot be used in service where the presence of precipitated wax would be a nuisance, e.g., for the lubrication of refrigerating compressors, particularly those of the Freon type.

Catalytic de-waxing processes have been developed recently (254, 265). Low oil pour-points are achieved by isomerisation and hydrocracking of constituents with long alkyl-chains at about 360 °C and pressures up to 10 MPa, in the presence of hydrogen and hydrogenation catalysts (Pt, Pd, Ni, etc.) on acidic molecular sieves with pores which allow the adsorption of straight-chain hydrocarbons, e.g., monoterpenes in the H-form. Light oil-cuts, e.g., from HP-hydrogenation, are suitable feed-stocks, and the product - obtained in 70-80% yields - has pour-points down to -40 °C and lower. The by-products are gases and light liquid hydrocarbons.

### Lubricant Base Stocks

The processes described earlier are used for the production of base oils for several different types of lubricating oils. These oils are nowadays regarded as being sorted into conventional types, and essentially classified under three group headings, each group being capable of further improvement with additives:

- A. High viscosity index raffinates, designed mainly for high quality engine oils and some special types of industrial oils (Table 3.6).
- B. Medium viscosity index raffinates, used either alone or in blends with the above oils for high quality industrial oils and greases (Table 3.7).
- C. Low viscosity index raffinates, suitable for some types of industrial oils, where the viscosity-temperature characteristics need not be considered and where thermooxidative stability is not decisive (Table 3.8).

### 3.2.2 Synthetic Oils

Although modern types of mineral oils reinforced by additives are capable of meeting a broad range of lubricating and other requirements, their properties are in some cases significantly surpassed by those of synthetic oils, for example, where very low or very high temperatures prevail, or under conditions where a wide operating temperature range or an unconventional environment, e.g., self-ignition hazard or exposure to ionising radiation, impose unusual requirements (30, 31, 32). Notwithstanding their limited availability and high price, there are fields where synthetic oils find application and are economically viable. Some types of synthetic oils are suitable for use in admixture with mineral oils - the so-called "semi-

Table 3.6. High Viscosity Index Raffinates

Parameter	Solvent Neutrals <sup>a</sup>							Brightstocks <sup>1</sup>	
	100	150	200	350	400	500	600	100BS	150BS
Viscosity at 100 °C (mm <sup>2</sup> .s <sup>-1</sup> )	4.1-4.6	5.2-5.6	6.3-6.7	9.2-9.6	10.0-10.5	12.3-13.5	14.2-15.0	20.0-21.2	31.5-32.5
Viscosity Index (min.)	100	97	97	95	95	95	95	95	95
Flash-point									
(P.M., °C, min.)	190	200	215	220	230	230	240	255	265
(O.C., °C, min.)	230	230	240	245	250	250	260	280	295
Fire-point (°C, min.)	245	245	265	270	275	275	300	320	320
Pour-point (°C, max.)	-17	-15	-12	-9	-9	-9	-9	-9	-9
CCT (% wt, max.)	0.02	0.03	0.05	0.1	0.1	0.1	0.15	0.6	0.8
Colour (ASTM, max.)	1.5	1.5	2.0	2.5	3.0	3.0	3.5	6	6
Colour stability <sup>11</sup>									
(48 h, 100 °C, max.)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Acidity (mg KOH/g, max.)	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Ash (% wt, max.)	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Clouding by separated paraffins after 3 months at 20-25 °C	-	-	-	-	-	-	-	no haze produced	

<sup>a</sup> Conventional term for fully-refined oils of low acidity; the numbers represent average values of viscosity in SSU at 37.8 °C.

<sup>1</sup> Conventional term for raffinates from deparaffined petroleum distillate feedstocks.

<sup>11</sup> Description of oil colour at 100 °C after 48 hours exposure to light.